PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLIS	HED	UNDER THE PATENT COOPERATION TREATY (PCT)
(51) International Patent Classification ⁶ :		(11) International Publication Number: WO 98/56881
C10M 173/02 // (C10M 173/02, 133:06, 133:06, 133:16, 135:10, 137:02, 145:14, 145:36), C10N 40:00	A1	(43) International Publication Date: 17 December 1998 (17.12.98)
(21) International Application Number: PCT/EI (22) International Filing Date: 12 June 1997 (71) Applicant: LAPORTE ESD LIMITED [GB/GB] House, 103 Wigmore Street, London W1H 9AB ((74) Agent: MAIWALD, Walter; Maiwald & Partner, Political	; Natio	BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR,
(54) Title: AQUEOUS LUBRICANT COMPOSITION ((57) Abstract	COMPR	ISING A MONOAMINE

The invention is directed to an aqueous lubricant concentrate composition which is usable for the preparation of an aqueous lubricating solution for lubricating conveyor belts and conveyor chains in the food and beverage industry. The composition comprises at least one monoamine compound as the main lubricating agent; an effective amount of a deposition—preventing component capable of preventing the deposition of solids from the lubricating solution under lubricating application conditions at least to such an extent that said lubricating application is not impaired by such depositions, without impairing the lubricating film—forming properties of the aqueous lubricating solution, and optionally further comprises a disinfectant, and other customary additives.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL A	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM A	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia .
AT A	Austria	FR	France	LÜ	Luxembourg	SN	Senegal
	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ A	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA B	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB E	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE .E	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF E	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG E	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ E	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY E	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA C	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG C	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH S	witzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI C	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM C	Cameroon		Republic of Korea	PL	Poland		
CN C	China	KR	Republic of Korea	PT	Portugal		
CU C	Cuba	KZ	Kazakstan	RO	Romania		
CZ C	Czech Republic	LC	Saint Lucia	RU	Russian Federation		•
DE C	Germany	LI	Liechtenstein	SD	Sudan		
DK D	Denmark	LK	Sri Lanka	SE	Sweden		
EE E	Istonia	LR	Liberia	SG	Singapore		

AQUEOUS LUBRICANT COMPOSITION COMPRISING A MONOAMINE

5

The invention relates to lubricant compositions which derive their lubricating properties from monoamines, especially coco-monoamines, and are suitable, in particular, for lubricating conveyor belts in the food and beverage industry. Specifically, the invention relates to such lubricant compositions free of soap.

In the food and beverage industry, e. g. in breweries or bottling operations at mineral water sources, bottle 15 cleaning, filling and labelling is carried out mainly by automation. As a rule, high-performance lubricants need to be used on the bottle conveyor facilities to quarantee problem-free conveying of the bottles. The filling performance of filling equipment has increased over the years as a result of technological progress. Requirements regarding the performance of the belt lubricants have increased correspondingly. In parallel, greater environmental awareness of the users has resulted in a demand for more environmentally and userfriendly chemicals 25 particularly when these are sprayed openly in premises, as is the case with belt lubricants, and where the lubricant liquid dripping off the belt may pass directly into the effluent (waste water) from the plant.

30 In the art, soap-based lubricants have many times been suggested, and are in general use today.

A major disadvantage of soap-containing lubricants is their sensitivity to hard water. Soaps tend to react with water

35 hardness forming salts (mainly Ca²⁺ or Mg²⁺ salts), to form the so-called lime soaps which are difficult to dissolve or even insoluble and strongly reduce the lubrication performance of the lubricant. Frequently, this leads to the formation of deposits on the conveyor belts and finally to

- 2 -

operating problems. To avoid this precipitation of lime soap, strong complexing agents (such as EDTA) are added to soap-containing lubricants or the application needs to be restricted to very soft water (which, however, is not generally available). For ecological reasons, the use of strong complexing agents in lubricants which pass into the waste water discharged from the plant is undesirable, since these complexing agents have poor biological degradability. EDTA especially is practically not biodegradable.

10

Soap-based lubricant also have other disadvantages, since they can promote the proliferation of germs and other microorganisms.

- 15 There have been attempts in the art at solving these problems, through alternative lubricants which comprise no soap. Generally, these alternative lubricants attempt to replace soap with specific amino compounds.
- 20 In EP-B1 0 044 458, a soap-free lubricant composition is disclosed which contains no complexing agent. The lubricant composition comprises alkyl polyether carboxylic acid salts combined with acyl sarcosinates.
- 25 From EP-B1 0 260 508, a method for lubricating a conveyor belt is known, which comprises the steps of lubricating the belt with a soap-free lubricant based on neutralized primary fatty amines, and cleaning the belt with cationic cleaning agents or organic acids. The reason for this is
- 30 that the amines used for lubrication form precipitates with anions, which strongly reduce the lubricating effect and can clogg spray nozzles etc.
- From EP-B1 0 372 628 and EP-A1 0 538 916 another substitute for soap-based lubricants is known, which is based on di35 or polyalkyl amines or corresponding di- or polyalkyl

aminoalkyl carboxylic acids. The aqueous lubricating solutions made from these compounds are used at pH-values between 5 and 8.

5 EP-B1 0 384 282 (which has been consolidated with EP 0 593 420) discloses the use of secondary and/or tertiary amines and/or salts thereof in lubricating formulations for PET or PC bottles. Generally, the amines are used as such, without the addition of surfactant, complexing agent or cosolvent.

10

WO 94/03562 discloses the use of polyamine derivatives of fatty amines and/or salts thereof. It is claimed that these amines are per se not very sensitive to process water anions such as sulfate, bicarbonate etc. The examples show that the lubricants of WO 94/03562 were only tested at low alkalinity (pH below 8), and were not tested with respect to their water hardness resistance. As such, the fatty amine salt-based lubricants of this art would not be expected to provide sufficient lubrication combined with the absence of precipitation problems in hard water application.

In DE-C2 42 44 536, it is suggested to base a soap-free lubricant on mainly two components, one of which is an alkyl diamine, optionally neutralized with an organic acid, and the other of which is a polyether carboxylic acid. The lubricants can be used between pH 6.5 and 7. The lubricant solution is made from a corresponding concentrate by adding soft water.

30

In DE-A1 43 15 21 (and corresponding EP 0 623 666) of the present applicant, it has been suggested to prepare soapfree lubricants on the basis of polyamines, which can optionally be combined with organic acids, to adjust the pH of the concentrate to between 4 and 8.

PCT/EP97/03080 WO 98/56881

The fatty monoamines suggested in EP 0 260 508 provide a better lubricating effect, at comparable concentrations, than the di-, tri- and polyamines later suggested in the art, as above discussed. The di- and higher amines of the 5 younger art are more expensive than the monoamines of EP 0 260 508, since they are made from these monoamines. The diand higher amines of the younger art avoid some of the precipitation problems, in the presence of carbonate, sulfate and especially phosphate anions, which EP 0 260 508 suggests to deal with by an extra cleaning step.

Lubricating solutions based on diamines or higher amines can be used without the extra cleaning efforts described in

15 EP 0 260 508. However, diamines and especially higher amines create increased foaming problems, as compared with monoamines. One therefore generally has to use defoaming agents in such products, but even then, such products produce large amounts of foam in practical application.

20

10

An important parameter in determining the quality of any such lubricant is the sliding friction coefficient provided by the diluted lubricating solution as actually used. Generally, a sliding friction coefficient between 0.10 and 0.14, at customary amine concentrations of the order of 100 ppm in the actual use solution, is achievable with state of the art diamine and higher amine based lubricants. A value of 0.10 would be considered very good; a value higher than 0.14 would be considered unacceptable.

30

25

It would be much easier to reach sliding friction coefficients at around 0.10 or even smaller, with monoamines as suggested in EP 0 260 508, but at the necessary concentrations in the actual use solution, 35 reaction between monoamines and anions such as carbonate,

- 5 -

sulfate and phosphate is so massive and fast, already in the central dosing unit, that sieves and nozzles of the spray applicator system are clogged within very short.

- 5 Apparently, the steps suggested in EP 0 260 508, which require a lot of extra effort, especially in switching the spray system from lubricant to cleaning composition and back, have prevented the industry from adopting this approach. Rather, the trend over the last decade has been in developing new lubricants based on other amines, i. e. di-, tri- and higher amines, to deal with the precipitation problem.
- Against this background, it is an important object of this invention to provide an aqueous lubricating solution (and a concentrate for making this solution), which makes it possible to achieve sliding friction coefficients of 0.10 and less, as low as 0.08 and even down to about 0.06.
- 20 It is another important object of this invention to provide an aqueous lubricating solution (and a concentrate for preparing it), which uses monoamines as the lubricating agent without being sensitive to problems caused by deposits in the presence of anions such as carbonate,

 25 sulfate and phosphate.

It is a further important object of this invention to provide an excellent aqueous lubricating composition (and a concentrate for preparing it) at reduced cost, and

30 especially without any need for extra cleaning steps or the use of acidic or complexing cleaning solutions.

Further objects and advantages of the invention will be notable from the following discussion and description of preferred embodiments.

- 6 -

The invention focusses, like EP 0 260 508, on the use of neutralized primary fatty amines, which have excellent lubricating properties. It thus turns away from the accepted wisdom in the art, that the use of monoamines is best avoided, and di- and higher amines should instead be used.

Instead of permitting a certain build-up of solid precipitate deposits in the apparatus, then remove the lubricant solution from the system, add a cleaning solution to the system, dissolve the deposits and then again replace the cleaning solution by the lubricating solution, as in EP 0 260 508, the invention teaches to already prevent the formation of such deposits, and thus removes the need for dealing with them after they have started to build up in the apparatus.

To achieve this, the invention teaches to add a depositionpreventing component to the monoamine-containing lubricant. In the context of this specification, a deposition-20 preventing component can be a single chemical species or may comprise a plurality of such species. Especially, said component can be a mixture of two, three or more chemical components. Instead of "deposition-preventing component", terms like "deposit-preventing agent", "anti-deposition compound" and "dispersant" may be used, in the context of this invention. Such somewhat varying terminology reflects the great variability of the inventive lubricant addivites, and all these terms should be regarded as synonyms. As 30 suggested and claimed here, this deposition-preventing component is part of the aqueous lubricant concentrate composition, and is present in the concentrate when this is mix d with the process water, in the central dosing unit of the lubricant spray system. It would of course be possible 35 to, instead, add such a deposit-preventing agent

- 7 -

separately, in the central dosing unit, or add it to the process water, and such embodiments, while presently considered uneconomical, should be considered as equivalent embodiments of the invention's preferred embodiment that comprises both monoamine compound and the anti-deposit compound in the same concentrate.

In any case, the definition of the deposit-preventing compound or dispersant as used in this specification is that it either completely prevents the formation of solid precipitate, e. g. by neutralizing the anions before they can react with the monoamine content of the concentrate, or at least prevents the formation of aggregates of solid precipited particles, which aggregates would be large enough to be retained by sieves, or incapable of passing through nozzles. The agent is also capable of preventing the formation of deposits of such solids on sieves, in nozzles, etc. which would block or clogg said sieves, nozzles, etc.

20

The exact mechanism by which the invention achieves its objects is not yet completely clarified, and it is possible that several somewhat different mechanisms are involved, likely depending at least partly on the choice of deposit-preventing agent. It is thus possible that with some agents of the invention, no solid precipitate particles are ever formed, whereas in other cases, very small microparticles are formed which, however, are prevented from aggregating or agglomerating and/or from settling on sieves, in nozzles, etc., to form clogging deposits. In the most preferred embodiments it is however notable that the aqueous lubricating solutions, as made up ready for use, remain completely clear to the naked eye, i. e. do not at all get cloudy, at least over the usual residence times of

- 8 -

the aqueous solution in the apparatus and actually much longer, often for weeks.

It is therefore presently surmised, although the applicant 5 does not want to be bound to any specific scientific theory, that the anti-deposit compounds of the invention actually prevent the formation of particles big enough to be visible to the naked eye, although what appears to be clear solutions may in fact be micro-dispersions or microsuspensions.

10

One important class of deposit-preventing compounds as according to the present invention comprises tensides (other than soap), also known as surface active agents. 15 Conventional soaps are not to be understood as comprised by the term "tenside" in the context of this specification. Generally, the invention prefers anionic, non-ionic or amphoteric tensides, since these do not only suggest themselves for use with glass bottles, metal cans etc., but 20 also for use with PET and PC bottles, which show high sensitiveness to cationic tensides. Of course, where this is no problem, such as in the handling of glass bottles, cationic tensides can also be used.

25 One reason why the use of such tensides, combined with monoamines, to prevent the deposit of solid precipitates in the presence of anions, has not before been suggested, is probably that tensides generally counteract the formation of the necessary lubricating film on the conveyor belt or 30 conveyor chain. To achieve the necessary lubrication, a sufficiently thick and effective film of aqueous lubricating solution must be formed on the surface of the belt or chain.

- 9 .

Tensides, especially in high concentration, can weaken or even destroy this film, and thus reduce the lubricating effect of the amine.

5 The invention is thus also based on the surprising finding that in the presence of tensides, the harmful deposits are not formed from the reaction of monoamines and anions, while still, a highly efficient and persistent lubricant solution film is formed on the belt or chain.

10

Among the tensides which have been found to provide the desired effect, are ether carboxylic acids, fatty alcohol alkoxylates, and a variety of amphoteric substances such as amphoteric alkyl monoamine or polyamine carboxylates,

15 betaines, sulfobetaines and the like. Details will be discussed hereinafter, and are also the subject matter of various of the attached claims.

One important aspect of the invention is that tensides
which per se show no anti-deposition effect, and which are
uneffective when used alone, provide improved antideposition efficiency when combined with each other, to
form a multi-compound anti-deposition component. Thus, some
amphoteric, anionic and nonionic tensides have been tested
and found to have, per se, no pertinent dispersing or antideposition effect. However, when combined, they exhibit
excellent such effects.

The best inventive products presently known use dispersing systems comprising at least one amphoteric tenside combined with at least one anionic tenside and at least one nonionic tenside. In these, the relative content of anionic tenside(s) is often higher than that of nonionic tenside(s), and the content of amphoteric tenside is generally the lowest of the three.

- 10 -

The concentration of anti-deposition agent or compound in the concentrate is relatively high, generally higher than that of the lubricating amine agent. Often, it is about two times the concentration of the amine. It is preferred that it should not be higher than three times the amine concentration, to avoid negative effects on the lubricating film. Another consideration is that the addition of tenside generally reduces the lubricating effect of the amine.

Monoamines, especially coco-monoamine, provide even much lower friction coefficients (down to 0.03) in the absence of tensides. However, the concentration will be selected, in practise, to optimize the anti-deposition effect and this will be generally feasible without approaching harmful tenside concentrations.

Generally, it is also possible to achieve the invention's effect by the use of deposit-preventing compounds which are not tensides.

20 It is thus possible to use polymeric dispersants, i.e. relatively low molecular weight polymers derived from vinylic monomers. Such compounds are known as dispersants in e.g. the paper making industry, in sludge treatments etc. Generally, such dispersants comprise homopolymers and copolymers based on acrylic acid and its derivatives, with molecular weights ranging up to 100.000.

Another class of deposit-preventing compounds usable according to this invention is formed by organic or even inorganic substances which can react, with the anions in the process water, before the harmful precipitates formed by the reaction of these anions with the monoamines in the concentrate, are deposited. Examples of such deposit-preventing compounds are alkaline or base-forming agents, such as alkanolamines, e.g. triethanolamine, or low

molecular weight polyamines, e.g. hexamethylene diamine, capable of forming cations together with an acid component of the formulation.

5 The presently preferred embodiments use tensides (except soap) as the deposit-preventing compound. Such preferred embodiments will now be described in more detail.

The present most preferred embodiments of the invention use 10 a combination of (at least) one amphoteric, (at least) one anionic and (at least) one nonionic tenside as the depositpreventing component.

Herein, the amphoteric tenside can be selected from a

15 variety of compounds, especially those corresponding to one
of the following general formulae (I) - (III).

One preferred class of amphoteric tensides corresponds to the general formula (I)

20

$$\begin{array}{c}
R_1 - \begin{pmatrix} N - R_5 \\ | \\ R_4 \end{pmatrix} n \\
\end{array} (1)$$

wherein R₁ is a linear, branched, saturated or unsaturated alkyl residue with 8 to 22 carbon atoms, or a corresponding alkoxy residue; R₂ is H, Na, K or N(R₃), with R₃ = alkyl or hydroxyalkyl; R₄ is H, alkyl, hydroxyalkyl, R₅-COO-R₂ or

30

wherein R_5 is alkyl or hydroxyalkyl, n and m are integers 35 from 1 to 10 and x is an integer from 1 to 50.

More specifically, a preferred dispersant comprises an alkyl monoamine carboxylate corresponding to the general formula (I), wherein R_1 is cocoalkyl, R_4 is H, R_5 is ethylene, R_2 is H and n is 1.

5

Such alkyl monoamine carboxylates can be obtained under the tradename "Amphoram CP1" from CECA Atochem S.A., France.

The presently most preferred amphoteric tenside is an alkyl polyamine carboxylic acid corresponding to the general formula (I), wherein R₁ is cocoalkyl, R₂ and R₄ are H, R₅ is ethylene and n is 3. This product can be obtained under the tradename "Triamphoram CP1", also from CECA Atochem S.A.

15 An alternatively preferred class of amphoteric tensides comprises betaines of the general formula (II),

wherein R₆ is R₁ or R₁-CONH-(CH₂)_n, R₁ and n having the same
25 meaning as in formula (I), and R₇ and R₈ are equal or
different alkyl or hydroxyalkyl substituents. Of these
betaines, some compounds have been found to be specifically
advantageous. In these, R₆ is cocoalkyl and R₇ and R₈ are
hydroxyethyl, or R₆ is cocoamidopropyl and R₇ and R₈ are
30 methyl.

Such dispersants can be obtained under the tradenames
"Tegotain N192" from Goldschmidt, Germany, "Amphotensid B4"
from Zschimmer und Schwarz, also Germany, and "Amphoteen
35 24" from Akzo Nobel.

- 13 -

Also alternatively, the amphoteric tenside can advantageously comprise a sulfobetaine corresponding to the general formula (III)

5

$$\begin{array}{c}
R_7 \\
| \\
R_6 - N^+ - R_9 - SO_3
\end{array}$$

$$\begin{array}{c}
| \\
R_8
\end{array}$$
(III)

10

wherein R₆, R₇ and R₈ have the same meaning as in formula (II), and R₉ is linear or branched alkyl or hydroxyalkyl.

Preferably, R₆ is lauryl, R₇ and R₈ are methyl and R₉ is 2-hydroxypropyl, or R₆ is cocoamidopropyl, R₇ and R₈ are

15 methyl and R₉ is

2-hydroxypropyl.

Such sulfobetaines (or sultaines) can be obtained from Witco/Rewo Chemische Werke GmbH, Germany, under the tradename "Rewoteric AM HC", and from Rhone Poulenc, France, under the "Mirataine CBS" tradename.

The anionic tenside of the presently most preferred embodiment of the invention can broadly be selected from the class of anionic polyether compounds. Suitable such polyether compounds comprise alkyl polyether carbonic acids, alkyl polyether sulfates and sulfosuccinates, and alkyl polyether phosphates. Instead of an alkyl group, the polyether compound can have a comparable alkylamido group.

30

The most preferred anionic tensides are presently selected from alkyl polyether carbonic acids and alkyl polyether sulfates.

WO 98/56881

It is specifically preferred that the dispersant comprises an alkyl polyether compound corresponding to the general formula (IV)

 $R_{1}-[O-R_{10}]_{p}-O-(R_{11})-COO-R_{2}$ (IV)

wherein R_1 and R_2 have the same meaning as in formula (I), R_{10} and R_{11} are alkyl residues, and p is an integer from 1 to 20.

10

Especially, R_1 is oleyl, R_{10} is ethylene and R_{11} is methylene,

p is 5 to 9 and R2 is H.

15 Such dispersants can be obtained from KAO, Japan under the tradenames "Akypo RO 50" (m=5), "Akypo RO 90" (m=9), and "Akypo RLM 100".

As an alternative anionic tenside, the dispersant may 20 comprise a compound of the general formula (V)

$$R_1 - [O - (CH_2)_n]_m - OSO_3 - R_2$$
 (V)

wherein R_1 and R_2 have the same meaning as in formula (I), and n and m are integers from 1 to 10. More specifically preferred, R_1 is a natural, a Ziegler synthetic, or an oxosynthetic alkyl, n is 2, m is 1, 2 or 3 and R_2 is sodium.

Such compounds can be obtained from Manro Products Ltd., England, under the "Manro BES" tradename. A preferred product is "Tensagex DLM 970", obtainable from Hickson, England.

- 15 -

Suitable alkylpolyether phosphates comprise "Marlopor FC" from Hüls, Germany.

In another preferred class of anionic tenside, i.e. the alkyl polyether sulfosuccinates, a very advantageous product is "Tensuccin HM 935" from ICI, an alkylpolyethoxysulfosuccinate-disodium salt.

Suitable alkylamido polyether sulfosuccinates comprise 10 "Lankropol KS6" from Akcros.

The third element in the presently most preferred embodiments is a nonionic tenside. This can for example be a nonionic fatty alcohol alkoxylate, an alkylpolyglucoside or an alkylpolyether carbonic acid monoalkylolamide.

Preferred alkyl polyalkoxylates comprise "Synperonic LF/RA 30" from ICI, England, and "Plurafac LF 431" from BASF, Germany. Plurafac is a (-OCH₃)-terminated fatty alcohol alkoxylate.

Preferred alkyl polyglucosides can be obtained from Henkel, Germany, under the "Glucopon" tradename, especially as "Glucopon 600 CSUP".

Preferred alkylpolyethercarboxy-monoalkylolamides comprise KAO's product "Aminol A 15".

"Symperonic LF/RA 30" and "Pluarfac LF 431" are presently 30 most preferred.

Presently, the best inventive combination (as far as dispersing performance is concerned) comprises an amphoteric tenside like "Triamphoran CP1", an alkyl polyether carboxylic acid anionic tenside like "Alypo RO

50", and either an alkyl polyalkoxylate such as "Plurafac LF 431" or an alkyl polyether carboxylic acid monoethanolamide, such as "Aminol A 15". In these, there is generally a smaller amount (based on overall concentrate, with about 3% coco-monoamine and about 3,5% formic acid) of about 1% amphoteric tenside, combined with about 3% anionic and about 2% nonionic tenside.

It is not alway necessary to have all three (above10 discussed) types of tenside combined in the anti-deposit or
dispersant component.

Combinations of anionic and nonionic tensides can be very successful. Thus, a combination of an (anionic) alkyl polyether carboxylic, such as "Akypo RO 50" and a (nonionic) aklyl polyalkoxylate, such as "Plurafac LF 431" can exhibit an anti-deposition effect which lasts for more than one week, even without any loss of clarity.

- 20 Combinations of an amhoteric with an anionic, but without a nonionic tenside, may be successful, and so may combinations of an amphoteric with a nonionic, but without an anionic tenside.
- 25 Some of these may even be more successful than a combination of all three types, as the experiments reported hereinafter show. There appear to be strong influences both of the specific combination selected and the respective rations of individual tensides in the combination. It is presently not yet possible to give a general rule for the influence of all structural and quantitative parameters, on the dispersing effectiveness.

Generally, the relative amounts of monoamine lubricating 35 agent (or agents) and deposit-preventing compound (or

- 17 -

compounds) will be selected, so that the amount of dispersant is high enough to prevent deposit formation, but not so high that the lubricating film-forming properties of the diluted lubricating solution suffer. To achieve this, different dipersants may have to be combined to experimentally determine the best selection.

To advantageously influence the storage stability and flow properties of the lubricant concentrates, the formulations

10 may additionally contain solubilisers in the form of monoor polyhydric alcohols (usually lower aliphatic alcohols or
glycols) or polyalkyleneglycols.

The formulation will generally further contain a disinfectant, such as 4,4-Dimethyl oxazolidine.

20

As a rule, the pH of the concentrate is below neutrality. To achieve this, a suitable excess amount of acid, usually formic, acetic or lactic acid, is added.

For the preparation of the lubricant concentrates according to the invention, the individual components can generally be used in acid or salt form.

The appropriate amount of demineralised water is introduced into a mixing vessel equipped with a stirrer. Subsequently, the components in the acid or the salt form are added.

Generally, this takes the form of addition of a preformed concentrate comprising all components. However, it is of course possible to prepare an aqueous lubricant composition of this invention by adding the individual components to the water one by one.

The superior properties of the lubricant composition
35 according to the invention will now be shown in further

5

detail by way of the following examples, in association with the attached drawing. In the drawing

- Fig. 1 represents a diagramatic representation of a bottle conveyor facility on which the reported experiments were carried out
- Fig. 2 shows a graphic representation of the sliding friction coefficients achieved with different lubricants and lubricant compositions.

For the turbidity tests reported below, Ladenburg town
15 water (25° total German water hardness, 15° carbonate
hardness, 10° non-carbonate hardness) was used.

Examples 1 - 19

- 20 Concentrates were made up from 3% coco-monoamine; 3,5% formic acid; various deposition-preventing compounds at varying overall amounts, and as defined in the TABLE, plus completely demineralized water (to 100%). Percentages here and in the TABLE are based on total concentrate
- 25 composition.

Example	Amphoteric tenside	Anionic tenside	Nonionic tenside	Anti- deposition
				effect
	Total and the second		ı	
7	24 ILIAMPHOLIM	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
2		or our oditure an'c		
3		ı	5,6% Plurafac LF 431	1
4	4,2% Triamphoram CP	3% Akypo RO 50	•	‡
22	т -	3% Akypo RO 50	2,6% Plurafac LF	+ .
		4% akvno RO 50	2% Plurafac LF 431	++++
9	1	- True of	1 - 3	-
7	4,8% Triamphoram CP	•	2,6% Pluratac Lr 431	+
	1. To merchand CP 1	3% Akypo RO 50	2% Plurafac LF 431	++++
x 6	1% Triamphoram CP 1	3% Akypo RO 50	4% Glucopon 600 CSUP	++++
10	1% Triamphoram CP 1	3% Akypo RO 50	2% Symperonic LF/RH 30	++
	19 Triamphoram CP 1	3% Akypo RO 50	2% Aminol A 15	++++
11	Te It temprorement at			

12	1% Triamphoram CP 1	7,7% Tensuccin HM 935	2% Plurafac LF 431 +	++++
13	1% Triamphoram CP 1	4,3% Tensagex DLM 970	2% Plurafac LF 431 +	+++
14	1% Triamphoram CP 1	3% Akypo RLM 100	2% Plurafac LF 431 +	++
15	1% Amphoram CP 1	3% Akypo RO 50	2% Plurafac LF 431 +	+
16	2% Amphoteen 24	3% Akypo RO 50	2% Plurafac LF 431 +	++
17	2% Amphotensid B4	3% Akypo RO 50	2% Plurafac LF 431 +	4
18	1,3% Rewoteric AM HC	3% Akypo RO 50	2% Plurafac Lf 431 +	+
19	2,6% Triamphoram CP	3% Akypo RO 50	1% Plurafac LF 431 +	+ + +

The TABLE shows, for each example, the anti-deposition (or deposition-preventing) effect in terms of the turbidity (and, in case, precipitation) observed, when a 0.3% solution of the concentrate in Ladenburg town water was left standing. Turbidity was determined by inspection (non-apparative). The symbols in the corresponding column in the TABLE have the following meanings:

- 10 turbidity visible immediately;
 precipitates forming after 1 hour
 + strong precipitation, after 24 hours
 ++ strong precipitation, after 48 hours
 +++ some precipication after 96 hours
 15 ++++ no turbidity visible for 7 days, later
 some turbidity and little precipitation
 +++++ no or very little turbidity after more
 than 14 days
- 20 Compositions with at least four "+" would be regarded as commercially fully usable. Compositions with inferior test results may, however, also be suitable under corresponding conditions (e.g. where softer water is easily available).
- To determine the lubricating performance of lubricants according to the invention and their individual components, an in-house bottle conveyor facility was used, as is illustrated diagramatically in Fig. 1. The belt speed and the spray volume per unit of time were kept constant during the measurements. The lubricant solutions were prepared from said local (Ladenburg) town water (25° German hardness). A 0.3% aqueous solution (by weight) of the lubricant concentrate was used for the comparative measurements.

from said local (Ladenburg) town water (25° German hardness). A 0.3% aqueous solution (by weight) of the lubricant concentrate was used for the comparative measurements.

5

A lubricant composition according to the invention was made up (similar to Example 8 above) as follows:

Component

10

- A 3% Coco-monoamine
- B 1% Coco-(NH-CH,-CH,-CH,),-COOH
- C 3% Oley1-(O-CH₂-CH₂),-O-CH₂-COOH
- D 2% alkoxylated fatty alcohol, ether capped
- 15 E 3% formic acid, 85% in water
 - F 88% water, demineralized.

(pH < 7)

20 (A is "Armeen CD" from Akzo; B is "Triamphoram CP1" from CECA Atochem S.A.; C is "Akypo RO 50" from KAO Corp.,

Japan; D is "Plurafac LF 431" from BASF AG, Germany.)

For comparison of lubricating efficiency, several mono-, 25 di- and triamines were formulated without the inventive dispersant, as follows:

3% amine

3% acetic acid, 60% in water

30 84% water, demineralized

Fig. 2 shows the sliding friction coefficients of various application solutions (at 90 ppm amine) of mono-, di- and triamines, and of the inventive solution (similar to 35 Example 8). The sliding friction coefficient K represents a

- 23 -

measure of the performance of the lubricant and is calculated using the formula

K=F/G

5

K sliding friction coefficient

force measured on the measuring facility of the bottle conveying plant (Fig. 1)

G weight of the bottles used in the test.

10

The lower the sliding friction coefficient, the greater the lubricating effect. Fig. 2 clearly shows that cocomonoamine provides the lowest sliding friction coefficient (K = 0.03, glass).

15

However, coco-monoamine formulated without the inventive dispersant is unusable in practise, due to the above-discussed precipitation problems. With sliding friction coefficiency at K = 0.075 (glass) and 0.102 (PET), the inventive product similar to Example 8 is decidedly superior as compared to the di- and triamines, which presently form the industrial standard. An improvement of the order of 0.2 units in the sliding friction coefficiency in practise means a very relevant improvement.

25

The inventive monoamine-based products produce practically no foam in application. This is a major benefit, since the known and presently used di- and triamine-based products generate huge volumes of foam. These foams are very stable, and have to be removed by rinsing. This causes increased effort and expenditure, and also puts increased strain on the plant and municipal waste water systems.

30

35

CLAIMS

- An aqueous lubricant concentrate composition,
 usable for the preparation of an aqueous lubricating solution for lubricating conveyor belts and conveyor chains in the food and beverage industry,
 comprising at least one monoamine compound as the main lubricating agent;
- 10 further comprising an effective amount of a depositionpreventing component capable of preventing the deposition
 of solids from the lubricating solution under lubricating
 application conditions at least to such an extent that
 said lubricating application is not impaired by such
- 15 depositions, without impairing the lubricating filmforming properties of the aqueous lubricating solution, and optionally comprising a disinfectant, and other customary additives.
- 20 2. The concentrate according to claim 1, wherein the monoamine compound comprises at least one, preferably primary, fatty amine, such as a C_8 - C_{22} fatty amine, and especially a C_{12} - C_{18} fatty amine.
- 25 3. The concentrate according to claim 2, wherein the fatty amine comprises, and preferably substantially consists of, coco-monoamine compounds.
- 4. The concentrate according to any one of claims
 30 1 to 3,
 further comprising an acid, especially a lower alkyl

further comprising an acid, especially a lower alkyl carboxylic acids such as formic acid, acetic acid and lactic acid, in an amount at least sufficient to neutralize the amine content of the concentrate.

5. The concentrate according to claim 4, having a pH-value between 3 and 8, preferably between 4 and 7.

6. The concentrate according to any one of claims 1 to 5, comprising at least one tenside or surface-active agent (except soap) as the deposition-preventing component.

5

- 7. The concentrate according to claim 6, said component comprising at least two tensides selected from anionic, amphoteric and non-ionic tensides, at least one of said tensides being anionic and at least one of said tensides being amphoteric or nonionic.
- 8. The concentrate according to claim 6 or 7, said component comprising one (or more) amphoteric tenside(s), one (or more) anionic tenside(s) and one (or more) nonionic tenside(s).
 - 9. The concentrate of claim 6, said component comprising a cationic tenside.
- 20 10. The concentrate according to claim 7 or 8, wherein the concentrate comprises at least one of an amphoteric alkyl monoamine or polyamine carboxylic acid or carboxylate, or a betaine, especially an alkyl or alkylamido betaine or sulfobetaine.

. 25

- 11. The concentrate according to claim 7 or 8, wherein the concentrate comprises at least one of a non-ionic fatty alcohol alkoxylate, a fatty amine alkoxylate, an alkyl polyglucoside and an alkyl polyether carbonic acid monoalkylolamide.
- 12. The concentrate according to claim 7 or 8, wherein the concentrate comprises at least one anionic polyether compound, especially at least one of an alkyl polyether carbonic acid,

- an alkyl polyether sulfate,
- an alkyl polyether sulfosuccinate,
- an alkyl polyether phosphate or
- a corresponding alkylamido polyether compound.

5

13. The concentrate according to claim 10, wherein the deposition-preventing component comprises at least one compound of the general formula (I)

10

$$\begin{bmatrix}
 R_1 - \begin{pmatrix} N - R_5 \\ | \\ R_4 \end{pmatrix} n$$
(1)

wherein R₁ is a linear, branched, saturated or unsaturated alkyl residue having 8 to 22 carbon atoms or a corresponding alkoxy residue, R₂ is H, Na, K or N(R₃)₃, wherein R₃ is alkyl or hydroxyalkyl, R₄ is H, alkyl, hydroxyalkyl, R₅-COO-R₂ or

20

$$[(CH_2)_mN]_x-R_5-COO-R_2$$

 $|R_5-COO-R_3|$

 R_5 is alkyl or hydroxyalkyl, n and m are integers from 1 to 25 10, and x is an integer from 1 to 50.

- 14. The concentrate according to claim 13, wherein the deposition-preventing component comprises an alkyl amine carboxylic acid corresponding to the general formula (I) wherein R₁ is cocoalkyl, R₄ is H, R₅ is ethylene, R₂ is H and n is 1.
- 15. The concentrate according to claim 13, wherein the deposition-preventing component comprises an alkyl polyamine carboxylic acid corresponding to the general formula (I), wherein R₁ is cocoalkyl, R₄ is H, R₅ is

30

35

ethylene, R, is H and n is 3.

16. The concentrate according to claim 10, wherein the deposition-preventing component comprises a 5 betaine of the general formula (II)

$$\begin{array}{c|c} R_{7} \\ | \\ R_{6} - N^{+} - CH_{2} - COO^{-} \\ | \\ R_{8} \end{array}$$
 (II)

wherein R₅ is R₁ or R₁CONH-(CH₂)-_n, with R₁ and n having the same meaning as in formula (I), and R_7 and R_8 are equal or different alkyl or hydroxyalkyl substituents. 15

- 17. The concentrate according to claim 16, wherein R₆ is cocoalkyl and R₇ and R₈ are hydroxyethyl.
- 18. The concentrate according to claim 16, 20 wherein R₆ is cocoamidopropyl, and R₇ and R₈ are methyl.
 - 19. The concentrate according to claim 10, wherein the deposit-preventing component comprises a
- sulfobetaine corresponding to the general formula (III)

$$\begin{array}{c}
R_7 \\
| \\
R_6 - N^+ - R_9 - SO_3
\end{array}$$

$$\begin{array}{c}
R_7 \\
| \\
R_8
\end{array}$$
(III)

wherein R_6 , R_7 and R_8 have the same meaning as in formula (II), and R, is linear or branched alkyl or hydroxyalkyl.

20. The concentrate according to claim 19, wherein R₆ is lauryl, R₇ and R₈ are methyl and R, is

2-hydroxypropyl.

- 21. The concentrate according to claim 19, wherein R₆ is cocoamidopropyl, R₇ and R₈ are methyl, and R₉ is 2-hydroxypropyl.
- 22. The concentrate according to claim 11,
 wherein the deposition-preventing component comprises a C₈10 C₂₂ alkylolalkoxylate, especially a C₁₁-C₁₅-alkoxylate.
- 23. The concentrate according to claim 12, wherein the deposition-preventing component comprises an alkyl polyether compound corresponding to the general formula (IV)

$$R_1 - [O - R_{10}]_p - O - (R_{11}) - COO - R_2$$
 (IV)

wherein R_1 and R_2 have the same meaning as in formula (I), 20 R_{10} and R_{11} are alkylene and p is an integer from 1 to 20.

- 24. The concentrate according to claim 23, wherein R_1 is C_9 - C_{11} alkyl, R_{10} is ethylene, R_{11} is methylene or ethylene, p is 3 to 9 and R_2 is H.
- 25. The concentrate according to claim 23, wherein R_1 ist C_{16} - C_{22} alkyl or alkenyl, especially oleyl, R_{10} is ethylene, R_{11} is methylene or ethylene, especially methylene, p is 5 to 9, and R_2 is H.
- 26. The concentrate according to claim 12, wherein the deposition-preventing component comprises a compound of the general formula (V)

$$R_1 - [O - (CH_2)_n]_m - OSO_3 - R_2$$
 (V)

30

25

wherein R_1 and R_2 have the same meaning as in formula (I), and n and m are integers from 1 to 10.

- 27. The concentrate according to claim 26,
 5 wherein R₁ is a natural, Ziegler synthetic or oxosynthetic alkyl, n is 2, m is 1, 2 or 3 and R₂ is sodium.
 - 28. The concentrate according to any one of claims 1 to 5.
- wherein the deposition-preventing component comprises a polymeric dispersant, substantially without surface-active properties, e.g. a polyalkyleneglykole.
- 29. The concentrate according to any one of claims 1 to
 15 5,
 wherein the deposition-preventing component comprises
 cations formed from an alkaline or base-forming agent,
 especially an alkanolamine or low molecular weight
 polyamine, and an acid, said cations being capable of
 20 reacting with deposition-forming anions such as carbonate,
 sulfate and phosphate to form soluble or dispersible solid
 microparticle reaction products.
- 30. The concentrate according to claim 29,25 wherein the concentrate comprises organic acid salts of triethanolamine or hexamethylene diamine.
 - 31. The concentrate according to any one of claims 1 to 30, comprising (in weight-%, based on total concentrate):
- 30 0.1 to 99%, preferably 0.5 to 10% and most preferred 1 to 5% fatty monoamine compound,
 - 0.01 to 50, preferably 0.1 to 15% and most preferred 1 to 10% f the deposition-preventing component,
- sufficient acid, especially lower alkyl carboxylic
 acid, to provide a pH lower than 8 to th

concentrate,

- in case, further customary additives,
- and water.
- 5 32. The concentrate according to claim 31, comprising:
 - about 3% by weight coco-monoamine;
 - about 1% amphoteric alkyl mono- or polyamino carboxylic acid;
- 10 about 3% alkoxylated ether carboxylic acid;
 - about 2% alkoxylated fatty alcohol ether and
 - about 3% lower alkyl carboxylic acid.
- 33. An aqueous lubricant composition, especially for
 15 belt or chain conveyors in the bottling industry,
 comprising the concentrate ingredients defined in any one
 of claims 1 to 32 plus a major amount of water, and
 especially containing between 10 and 500, preferably about
 90 ppm of monoamine lubricating agent.

20

- 34. Use of the concentrate according to any one of claims 1 to 32, for preparing an aqueous lubricating solution, especially as defined in claim 33, wherein the concentrate contains from 1 to 30% by weight, based on
- 25 total concentrate, of a fatty monoamine lubricating agent, especially coco-monoamine and the lubricating solution has a sliding friction coefficient, at about 90 ppm monoamine concentration, of less than 0.10, preferably less than 0.08.

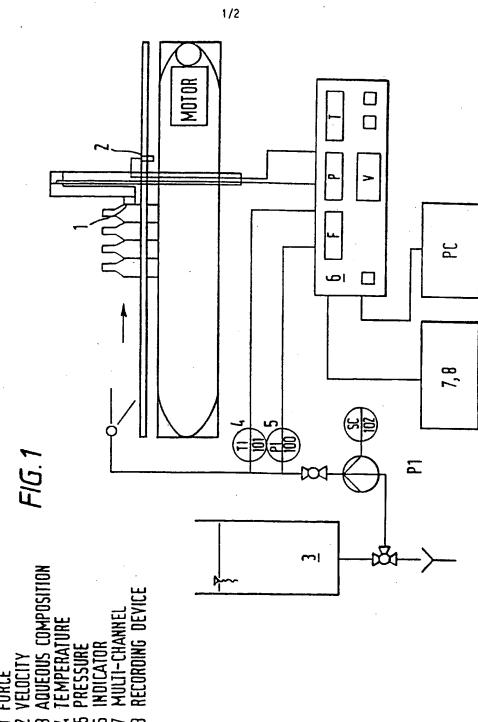
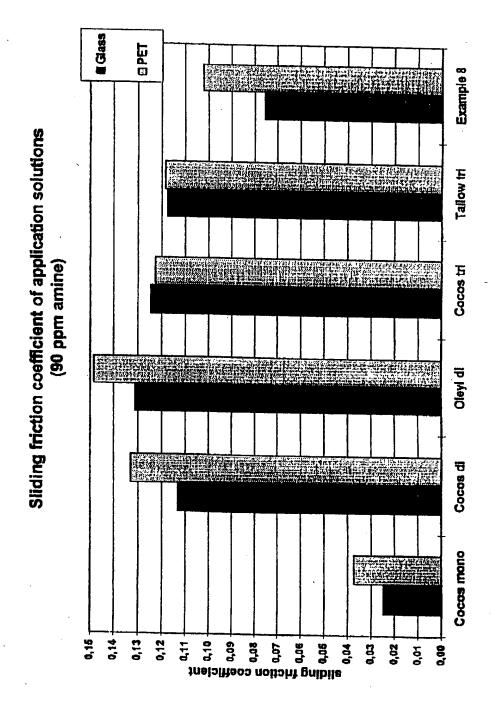


FIG. 2



INTERNATIONAL SEARCH REPORT

int .tional Application No PCT/EP 97/03080

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C10M173/02 //(C10M173/02,133:06,133:06,133:16,135:10,137:02, 145:14,145:36),C10N40:00 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C10M Documentation searched other than minimumdocumentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Citation of document, with indication, where appropriate, of the relevant passages 1-6,9,X EP 0 260 508 A (AKZO NV) 23 March 1988 cited in the application 28,29, 33,34 see column 3, line 5 - line 20 see column 3, line 38 - line 43 see column 4, line 36 - line 41 1-6, EP 0 372 628 A (AKZO NV) 13 June 1990 X cited in the application 28-31, 33,34 see page 3, line 26 - page 4, line 9 see tables I,A,E,G -/--Patent family members are listed in annex. χl Further documents are tisted in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled "O" document referring to an oral disclosure, use, exhibition or other means in the art. "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of theinternational search Date of mailing of the International search report 25/02/1998 13 February 1998 Authorized officer Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Rotsaert, L Fax: (+31-70) 340-3016

INTERNATIONAL SEARCH REPORT

int ilonal Application No PCT/EP 97/03080

	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
ategory °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to daim No.
	WO 93 18121 A (HENKEL KGAA) 16 September 1993 see page 4, paragraph 4 - page 7, paragraph 2 see page 7, paragraph 4 - page 8, paragraph 2 see page 14, paragraph 3 - page 15, paragraph 1	1-11, 13-18, 22,33,34
X	DE 42 44 536 A (CLEANSO HYGIENE GMBH) 7 July 1994 cited in the application see page 2, line 31 - line 60	1-8, 10-18, 22-25, 28-34
Y	see examples 1-3	19-22, 26,27
1	DE 44 44 598 A (LAPORTE GMBH) 20 June 1996 see page 2, line 32 - page 3, line 45	19-22, 26,27
A	US 4 929 375 A (ROSSIO CHARLES E ET AL) 29 May 1990 see the whole document	1,33,34
<i>;</i>	-	

INTERNATIONAL SEARCH REPORT

Information on patent family members

In: tional Application No PCT/EP 97/03080

Patent document cited in search report Publication date				7 0 1 7 4 1 0 1 7 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
CA 1308379 A 06-10-92 DK 436787 A 20-03-88 US 4839067 A 13-06-89 EP 0372628 A 13-06-90 AT 150073 T 15-03-97 AU 623952 B 28-05-92 AU 4589689 A 07-06-90 DE 68906514 T 06-03-97 DE 68927864 D 17-04-97 DE 68927864 T 19-06-97 EP 0538916 A 28-04-93 ES 2040986 T 16-02-97 ES 2099199 T 16-05-97 HK 5995 A 20-01-95 JP 2194096 A 31-07-90 JP 7035516 B 19-04-95 SG 160194 G 28-04-95 US 5062978 A 05-11-91 WO 9318121 A 16-09-93 DE 4206506 A 09-09-93 AT 130361 T 15-12-95 CA 2131312 A 16-09-93 DE 59300967 D 21-12-95 EP 0629235 A 21-12-94 ES 2079966 T 16-01-96 US 5565127 A 15-10-96 DE 4244536 A 07-07-94 NONE DE 4444598 A 20-06-96 AU 5556696 A 03-07-96 WO 9618709 A 20-06-96 EP 0797652 A 01-10-97 US 4929375 A 29-05-90 US 5441654 A 15-08-95 US 5510045 A 23-04-96 US 5009801 A 23-04-991 US 5073280 A 17-12-91				
AU 623952 B 28-05-92 AU 4589689 A 07-06-90 CA 2004544 A,C 05-06-90 DE 68906514 T 06-03-97 DE 68927864 D 17-04-97 DE 68927864 T 19-06-97 EP 0538916 A 28-04-93 ES 2040986 T 16-02-97 ES 2099199 T 16-05-97 HK 5995 A 20-01-95 JP 2194096 A 31-07-90 JP 7035516 B 19-04-95 SG 160194 G 28-04-95 US 5062978 A 05-11-91 WO 9318121 A 16-09-93 DE 4206506 A 09-09-93 AT 130361 T 15-12-95 CA 2131312 A 16-09-93 DE 59300967 D 21-12-95 EP 0629235 A 21-12-94 ES 2079966 T 16-01-96 US 5565127 A 15-10-96 DE 4244536 A 07-07-94 NONE DE 4444598 A 20-06-96 WO 9618709 A 20-06-96 EP 0797652 A 01-10-97 US 4929375 A 29-05-90 US 5441654 A 15-08-95 US 5009801 A 23-04-96 US 5009801 A 23-04-96 US 5009801 A 23-04-91 US 5073280 A 17-12-91	EP 0260508 A	23-03-88	CA 1308379 DK 436787	A 06-10-92 A 20-03-88
AT 130361 T 15-12-95 CA 2131312 A 16-09-93 DE 59300967 D 21-12-95 EP 0629235 A 21-12-94 ES 2079966 T 16-01-96 US 5565127 A 15-10-96 DE 4244536 A 07-07-94 NONE DE 4444598 A 20-06-96 W0 9618709 A 20-06-96 EP 0797652 A 01-10-97 US 4929375 A 29-05-90 US 5441654 A 15-08-95 US 5510045 A 23-04-96 US 5009801 A 23-04-91 US 5073280 A 17-12-91	EP 0372628 A	13-06-90	AU 623952 AU 4589689 CA 2004544 DE 68906514 DE 68927864 DE 68927864 EP 0538916 ES 2040986 ES 2099199 HK 5995 JP 2194096 JP 7035516 SG 160194	B 28-05-92 A 07-06-90 A,C 05-06-90 T 06-03-97 D 17-04-97 T 19-06-97 A 28-04-93 T 16-02-97 T 16-05-97 A 20-01-95 A 31-07-90 B 19-04-95 G 28-04-95
DE 4444598 A 20-06-96	WO 9318121 A	16-09-93	AT 130361 CA 2131312 DE 59300967 EP 0629235 ES 2079966	T 15-12-95 A 16-09-93 D 21-12-95 A 21-12-94 T 16-01-96
W0 9618709 A 20-06-96 EP 0797652 A 01-10-97 US 4929375 A 29-05-90 US 5441654 A 15-08-95 US 5510045 A 23-04-96 US 5009801 A 23-04-91 US 5073280 A 17-12-91	DE 4244536 A	07-07-94	NONE	
US 5510045 A 23-04-96 US 5009801 A 23-04-91 US 5073280 A 17-12-91	DE 4444598 A	20-06-96	WO 9618709	A 20-06-96
	US 4929375 A	29-05-90	US 5510045 US 5009801 US 5073280	23-04-96 A 23-04-91 17-12-91